Laser Spectroscopy of Mineral Particle Surfaces:
Phase I. Feasibility Study

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Final Report

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Summary

Experiments were carried out in keeping with the Statement of Work given in Appendix A of the above named Contract. All objectives were achieved.

Measurements of fluorescence of the surface with and without an adsorbed dye and micro Raman effect were done on model compounds, quartz, alumina and gypsum. At least one of the above techniques was successful in each case although not all methods worked well on all samples. It was found possible to identify individual particles in finely ground (50-200 μM) mixtures. A marked difference was found between samples of gypsum, one of which had been doped with Radium.

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Introduction

The identification of minerals at the surfaces of fine grains of agglomerated, compacted, intruded or weathered particles is of importance in understanding the mineralogical distribution of trace elements. For example, the study of the chemical speciation of readsorbed radioactive contaminants (e.g. radium and thorium) in uranium mine tailings would benefit greatly from a detailed knowledge of the surfaces. Unfortunately, the identification of minerals in fine particles is very difficult in such samples, and such techniques as x-ray diffraction, and x-ray fluorescence have poor spatial resolution, while the micro-beam methods of scanning Auger microscopy and secondary ion mass spectroscopy give elemental but not structural information.

Recent discoveries in this laboratory have shown that the fluorescence spectra of certain doped mineral surfaces show characteristics which will assist in the identification of chemical compounds and minerals on the surfaces. This experiment can be performed by the use of a laser beam, which can be focussed to a diameter of less than 1 micron. It thus seemed possible to obtain a detailed map of the chemical composition on such surfaces. It could be anticipated that the lattice-dopant interaction would be affected by only the outermost atomic layers so that effects of weathering and process alteration might also be observed.

The interaction between a molecule and a surface can be

classified into two general categories: physical adsorption and chemical adsorption, or chemisorption. When a molecule is chemisorbed onto a surface, the strong interaction can influence the molecular properties such that spectral changes can be observed. For instance, vibrational frequences of the normal modes that represent the groups of atoms involved in the direct attachment to the surface can shift or the spectral bands can broaden. In the spectral domain of electronic spectroscopy, one can also observe band shifts and changes in the spectral contours similar to those found in vibration spectroscopy. The above spectral observations all suggest that the molecule is experiencing a different chemical environment relative to the gas phase where interactions are almost negligible. It is this phenomenon, spectral responses to strong molecule-surface interaction, that we wish to utilize in order to identify unknown surfaces by observing the induced fluorescence emitted by the probe molecule on the surface. As was stated in the interim report, we chose the porphyrin dye family as proble molecules since the lifetimes of the molecules in their first excited singlet state range from approximately five to twenty nanoseconds in solution and therefore should be within our detection capabilities when deposited on a surface.

Under the present Contract, we have explored and assessed the application of focussed laser beams in making the identification of mineral particles. Using these focussed beams, we have used the microscopic techniques of fluorescence spectroscopy and Raman scattering, for mineral surface

identification. These techniques use the same apparatus, which is a microscope coupled to a spectrometer-detector-signal processing system. The advantage of this system is the high spatial resolution that can be achieved on a surface (< 1 μm) and the subsequent collection of spectral data from the illuminated area. The basic difference in the two techniques is in the mode of sample illumination. The microfluorometric system uses a nanosecond pulsed laser to probe the sample. Here, the sample surface is prepared with fluorescent dye molecules and the laser induced fluorescence which is collected with the microscope objective can be analyzed with respect to intensity, frequency, time decay. Both the frequency spectrum and the time decay of the fluorescence are parameters of the dye molecule that are very sensitive to the chemical environment. Therefore surface identification can be achieved by the use of a data base which consists of frequency-time data on systems of dye molecules on known minerals.

Using the same experimental set up, we have also been able to assess the natural fluorescence of the undoped surfaces as a possible second technique. The combination of the two techniques will prove important in cases of a) minerals which do not naturally fluoresce and b) minerals of low surface area which do not adsorb much dye. For minerals which fail both these criteria still another method must be used.

This third technique, micro-Raman scattering, requires no sample preparation and in contrast to the pulsed laser illumination of the fluorescence technique described in the above

paragraph, this type of spectroscopy uses a continuous wave Argon ion laser and appropriate signal processing systems. The spectral information that can be obtained with this system is intensity vs frequency spectra of the component molecular vibrational modes for the various minerals. These data can perhaps be used as a fingerprint identification of the individual minerals that are suspected to be present in the sample.

The set of tasks addressed in the present project was designed to test the feasibility of the concept. The specific objectives set out were:

1. Development of experimental techniques to prepare a thin layer of the dopant dye on the model compounds chosen, silica and alumina, both as pure compounds and as mixtures.

2. Laser spectroscopic measurements on the prepared surfaces of the model compounds. The measurements should include laser fluorescence, fluorescence lifetimes and laser Raman on pure compounds and on mixtures. A strong effort should be made to ensure the reproducibility of the spectra.

3. Spectral analysis and interpretation of the spectra obtained from the model compounds.

4. Application of the preparation technique to appropriate mineral speciments, both as pure minerals and as mixtures.

5. Laser spectroscopic measurements and spectral interpretation on the mineral specimens.

6. Preparation of mixtures of pure minerals and trace elements, such as quartz and alumina in major proportions. with gypsum as a trace constituent. The gypsum should contain Ra-226, in sufficient quantity so that the resultant mixture is of the order of 100 pCi/g in Ra-226.

7. Laser spectroscopic studies, including interpretation, on the material prepared in item 6.

We are pleased to report that all of these tasks have been successfully performed and that each of the objectives has been achieved with one technique or another.

Section II-Experimental

A. Materials

The minerals recommended by the Scientific Authority were Quartz, Alumina and Gypsum. These were obtained in two grades, to obtain different specific surface areas:

Silica Gel (70-230 mesh; 70-200 μm)
surface area 500-600 $m^2\ g^{-1}$ as specified by the manufacturer, Davison Chemical Co.

α Quartz from the Carleton University mineralogical collection, $\sim 2 m^2\ g^{-1}$

γ Alumina (Neutral grade 70-200 μm)
Woelm Pharma, Activity Grade I, stated to have an area of 200-300 $m^2\ g^{-1}$. Used with no further dehydration or reactivation.

α Alumina (Corundum) from the Carleton University mineralogical collection $\sim 2 m^2\ g^{-1}$.

Gypsum from the Carleton University mineralogical collection, crushed by hand and sorted as to size $\sim 2 m^2\ g^{-1}$.

The solvents used for this dye deposition were 1,2 Dichloroethane (Anachemia Chemicals Ltd. UV Spectrophotometry Grade) and Chloroform (Caledon Laboratories Ltd. ACS Spectro Grade). Both were used without further purification. The dye deuteroporphyrin IX Dimethyl Ester was obtained from Porphyrin Products Inc. with a purity greater than 97% based on spectral data and HPLC analysis. Several surfactants were obtained:

Oleic Acid ($C_{17}H_{33}COOH$), The British Drug Houses Ltd., Nacconal-NRSF (alkyl Benzene Sulfonate C_{12}-C_{18}), Allied Chemical, Aerosol-OS (Sodium Alkyl Naphthalene Sulfonate) American Cyanamid, 1-Naphthoic Acid Aldrich Chemical Co., Inc., N-Butanol (Certified ACS) Fisher Scientific Co. and Heavy mineral oil. For the ^{226}Ra additions, a ^{226}Ra standard solution, certified 1968 NBS 49.5 C sample was diluted with 0.1 M HNO_3 such that 1.00 ml contained 480 pC ^{226}Ra.

B. Sample Preparation

Both the high and low surface area minerals were coated with the dye for the micro-fluorescence experiments by several procedures. First, 10 mg of the mineral is covered with 1 mL of the solvent 1,2 dichloroethane then 50 µL of a 1.0×10^{-4} M dye solution is added. This amount of dye solution gives approximately 10% surface coverage of the high surface minerals. Next the sample is placed in a vacuum desiccator and the solvent is removed. In the second procedure, 1 mL of the solvent (1,2 dichloroethane or chloroform) is used to cover 10 mg of the mineral. Then, 50 µL of a 1.0×10^{-4} M surfactant solution is added. 1,2 dichloroethane is the solvent for the oleic acid and chloroform dissolves the remaining surfactants. Again the solvent is removed under a vacuum. To the dry minerals which have been covered with the surfactant, 1 mL of the appropriate solvent is added along with 50 µL of the dye solution, and the solvent is again removed in the vacuum desiccator. At first, we used glass vials to hold the dye-surfactant-mineral mixtures but

we found that the glass was competing with the mineral for the dye film. At this point, we changed to Teflon beakers which reduced the loss of dye to the container surface.

Using the ^{226}Ra HNO_3 stock solution described in the above section, the following procedure was used to incorporate the ^{226}Ra into the gypsum. 1.00 ml of the ^{226}Ra solution was diluted to 100 ml with distilled water. In the case of the blank, 1.00 ml of 0.1 M HNO_3 was diluted to 100 ml. 1.00 g of crushed gypsum was added to a 250 ml Teflon beaker containing a magnetic stirring bar. The ^{226}Ra solution was added and the beaker covered with parafilm. The beakers were placed on a magnetic stirrer with an asbestos pad under them to minimize heat transfer from the stirrer. The speed of the stirrer was set so that the crystals of gypsum were continuously moving. A 1.0 mL aliquot of the liquid was taken at 1, 2, 4, 6, 24 and 48 hours by using a glass pipet punched through the parafilm. The stirring was not stopped. No sample was taken from the blank. Each 1.0 mL sample was analyzed for ^{226}Ra. This was done by first increasing the volume to 25 mL with 0.1 M HNO_3 and then adding 1.00 mL ^{133}Ba as a tracer. 1.00 mL Ba^{2+} was added followed by 0.5 mL of 9 M H_2SO_4 to precipitate the ^{226}Ra with $BaSO_4$. After standing for 30 min. the solution was filtered through a 0.45 μm membrane filter. After drying, the filter papers were measured in the γ spectrometer for ^{133}Ba and the α spectrometer for ^{226}Ra

activity. The percent recovery of ^{133}Ba was used to determine recovery of ^{226}Ra in the solution. The amount of ^{226}Ra incorporated was determined by difference. An additional sample was taken after 53 hours although the stirring had been stopped at 48 hours. Gypsum crystals treated with ^{226}Ra were recovered from the solution by filtering through a 0 .45 μm membrane filter and were air-dried. Duplicate samples and a blank were run.

For the micro-Raman experiments, no dye-surfactant film was necessary because the Raman method can produce spectra of the natural mineral surface.

C. Apparatus

1. Micro-Fluorescence

The laser system used for the present experiments is composed of a flowing gas N_2 laser which is coupled to an organic dye laser to produce continuous lasing over a wide spectral range. The N_2 laser, a Lambda Physik model M2000 produces a light pulse with a 4 ns width and approximately 1 MW peak power every 40 m sec. This laser is used to pump a Lambda Physik FL 2000 dye which includes one amplifier stage. Relevant characteristics of the laser system are a high conversion efficiency (~10%) for dyes which produce stimulated emission in the spectral range of 355-755 nm and spectral bandwidth of approximately 1 cm^{-1}. Using a prism to separate the superradiance of the dye from the laser beam and the various mirrors in the optical systems, 0.5 mW of average laser power was

measured at the entrance of the microscope. This power level was maintained throughout the experiments.

The system used to detect the fluorescence emitted from our samples must be capable of detecting and processing very fast light pulses. Whether the radiation originates from reflected laser light or induced spontaneous fluorescence from a probe dye molecule, the detection system must be able to follow in time a radiation pulse with a rise time $\leq$ 2 ns. For the present experiments, a further limitation placed on the detector is the spectral detection range. When the porphyrin dye molecule is exposed to the laser radition, induced fluorescence is observed in the red domain of the visible spectrum. Thus, a detector which is red sensitive would give a maximum signal to noise ratio for our experiment. Our choice which would optimize the time and spectral performance of the equipment is the RCA-7102 photomultiplier tube (PMT). The technical data sheet for this PMT lists the following: (1) 10 stage, Head-on type with a S-1 response (Visible and Near-Infrared Regions - 7600 Å maximum sensitivity); (2) Tube voltage 1200 V DC; (3) Typical current amplification 1.5×10^5; (4) Typical anode-pulse rise time - 2.4 ns. In addition to the gain obtained in the PMT ($\times 10^5$) we used two LeCroy VV 101 A ultra wideband pulse amplifiers to enhance the observed signals further. The effective gain in this stage was measured to be 60-90.

Finally, the output from the PMT and the LeCroy amplifier was processed in a Princeton Applied Research Model 162 Boxcar Averager System Main Frame. To the main frame, a Princeton Applied Research Model Gated Integrator was added. Thus, the overall capabilities of this system are: (1) processing low repetition rate signals (25 Hz), (2) narrow time aperature durations (2 ns in the present experiments) and (3) time scanning of the 2 ns aperture so that rapid decay of the spectral emission can be recorded.

The main optical component of the experiment is a Zeiss Winkel microscope which we have modified to illuminate and collect experimental data from a small particle with the same objective lens. The functions of this geometry are (1) to focus the laser beam to small diameter ($\sim$1 μm), (2) to collect the induced phenomena from the same spatial region. and (3) to observe spectra from small particle sizes 2 μm or larger. To avoid laser induced damage on the particle surface, it was necessary to use a 10X objective (Zeiss Winkel) with a numerical aperature of 0.25, a focal length of 14.8 mm, and a free working distance of 7.10 mm. Besides the above optics, the complete system utilized various mirrors and prisms to steer the laser beam and collect the radiation from the sample. See Figure VI for a schematic diagram of the experimental apparatus.

2. Micro Raman Spectroscopy

For the micro Raman experiments, we used a Coherent Radiation continuous wave super graphite argon ion laser. The

total laser output for all laser lines is 4 watts, but our experiments require a single laser line therefore we installed a tuning prism in the laser cavity and selected the 488.0 nm exciting line. Laser power of this line is 1.4 watts. In order to eliminate non-lasing radiation from the laser beam, we placed a 1Å narrow band interference filter in the beam path. As a result, the laser power was decreased by 50%. If we also reckon with the 90% loss of laser power in the beam splitter of the microscope, we find that a total of 63 mW of laser power was available to excite the Raman scattering in the sample. This power level was more than sufficient to obtain good spectra.

Since the laser used in these experiments is a continuous wave laser, a different signal processing system is required to acquire the data. The output of the PMT (ITT FW 130 16 stage end-window type: Gain - 5×10^6; tube voltage - 1800 DC; Spectral response maximum - 4000 Å) is sent to a Princeton Applied Research Model 1120 Amplifier-Discriminator. This unit is a high gain, low noise amplifier followed by a fast tunnel diode discriminator. Amplifier gain of more than 2000 is accomplished through use of four current mode stages in cascade. Next, the amplified signal pulses are counted with a Princeton Applied Model 1105 Data Converter. This unit is basically a high speed rate meter that can process the signals from the 1120 amplifier. Also, the 1105 has a very large dynamic range in counts/sec (10 - 10^6 c/s) and X1, X10, X1000 prescaler is provided for scale expansion and extension of zero supression. All output is then recorded on a chart recorder.

The optical illumination and collection of scattered light is accomplished in the same manner as in the micro-fluorescence experiments mentioned above with the following exception. A Wild achromatic dry 40X objective was used. This 40X objective has the following specifications, (1) 0.65 numerical aperature, (2) focal length 4.3 mm, and (3) a free working distance of 0.54 mm.

Section III-Results and Discussion

We have completed experiments in several series:

A. Microfluorescence
   - i) Dye reference solution spectra
   - ii) Direct adsorbed dye spectra
   - iii) Indirect adsorbed dye spectra
   - iv) Temporal data
   - v) Mixed samples

B. Micro Raman spectra

A. Microfluorescence

i) Dye reference solution spectra.

In the present study, we measured the spectral properties of the deposited probe molecule relative to its properties in solution. For deutroporphyrin IX dimethyl ester in 1,2 dichloroethane, the absorption spectra show the usual Soret band at 398 nm and four bands at 496, 527, 564 and 620 nm. This latter band system is known as the Q band region in porphyrin spectroscopy, and is very sensitive to the chemical environment

of the molecule. The laser induced fluorescence spectrum from the 1,2 dichloroethane solution has bands at 622.5, 650.0 and 686.5 nm where the bands at 622.5 and 686.5 nm correspond to the 620.0 and 564.0 nm bands in the absorption spectrum respectively. This correlation between the most red-shifted absorption bands and the observed emission bands is common in organic dyes where hot fluorescence is not usually observed. Therefore, we can assign the 622.2 nm band as the 0'-0 electronic transition with the 686.5 nm band as the 1'-0 vibronic transition. We will maintain this assignment throughout the following discussion except the wavelengths for the transition will change from sample to sample. Another band was observed at 650.0 nm, and we can only make a speculative assignment at this time. We think owing to its short lifetime relative to the main fluorescence at 622.5 nm that the molecular species responsible for the emission is an oxygen adduct of the porphyrin. More experiments are needed to confirm this assignment.

Another solution used was the oleic acid-dye mixture, whose the emission maxima occurred at 627.5, 644.5 and 688.4 nm, very similar to 1,2 dichloroethane solution. The above data represent our probe molecule's characteristic parameters in the spectral domain. These parameters reflect the unique chemical environment of the dye molecule by exhibiting slight shifts in the bands. These experiments give us very useful information about the dye molecule system especially in the large amount of fluorescence detected, but an observation of strong fluorescence in solution does not necessarily mean that one will find fluorescence when the molecule is adsorbed on a surface.

ii) Direct adsorbed dye spectra

This first series of experiments consisted of a deposition of dye molecules directly on a silica gel surface (500-600 m^2/g). 50 µl of the 1.0×10^{-4} M dichloroethane solution was used. When the sample was placed under the microscope and exposed to the laser radiation, no visible fluorescence was observed. If one tries the same experiment with the solid dye sample (small flakes as obtained from the commercial source), again no fluorescence results. The fluorescence in the solid state is quenched and can not be observed with the present apparatus, consequently the dye on the silica gel surface must be in a state similar to that in the pure solid.

Since the dye is fluorescent in solution, we decided to cover the silica gel-dye surface with a heavy mineral oil. The dye molecule would now experience a solution layer and should become fluorescent. Positive results were obtained with dye emission bands observed at 597.8 and 660.4 nm. We also observed fluorescence at 617.8, 643.0 and 681.8 nm from the γ-Al_2O_3 sample. Our ultimate goal was to extend this procedure to the low surface area minerals quartz, corundum and gypsum. When we tried to coat these minerals with the same procedure, the fluorescent dye layer began to dissolve from the surface. This fact was evident in the overall increase in fluorescence signal as the experiment progressed. Therefore, we had to devise another method to coat these low surface area minerals.

iii) Indirect adsorbed dye spectra

Several surfactants were obtained (listed in Section II A) and every one, with the exception of oleic acid, gave a brown layer of dye on the mineral surface. A brown colour indicates a thin film of dye which does not remain stable when the mineral oil is added. This layer can also be removed in total with the solvent. When we used the oleic acid as the first layer and the dye as the second layer, all samples exhibited the pink colour that indicates a strong fluorescence should be observed. In Table I, we list all the observed spectral data obtained in the fluorescence experiments. The data can be divided into two groups. Group I consists of the high surface area minerals and Group II contains the low surface area minerals. If we compare the observed data of the silica gel (with oleic acid) and the γ- Al_2O_3 (with oleic acid), we find that larger differences exist in the wavelengths and therefore could be used as a unique identifier for the mineral. In the second group, all data are equal within experimental error and we conclude that the oleic acid-dye layer contains a majority of physically adsorbed species rather than chemisorbed. As a result of this observation, we cannot use this surfactant-dye combination for low surface area identification.

iv) Temporal data

The temporal data also confirms this conclusion. In Table II, we summarize the temporal data obtained from all of the

samples. For the oleic acid-dye solution, we found a lifetime of 19.9±2.9 ns for the emission at 623.0 nm. This lifetime would be typical for a thick layer of solutions in which no surface interaction is present. When the dye molecule does interact with the surface, the lifetime of the emission becomes shorter. This can be seen in the data for silica gel and γ-Al_2O_3 where the lifetimes are 6.3±1.3 ns and 8.9±1.2 ns respectively. These values are significantly different from the oleic acid-dye lifetime but for the low surface area minerals, a long lifetime was observed and these values are very close to the oleic acid-dye value. We could expect this result since the mineral spectral data were very similar to those from the oleic acid-dye spectrum.

v) Mixed samples

To identify a particular mineral in an unknown sample, a proper data base of spectral and temporal observation should be known. At this point, we have a data base for the two high surface area materials: silica gel and γ-Al_2O_3. Respectively, Figures I and II show the spectral data for the laser induced fluorescence of these samples.

To illustrate the identification of small particles, we take a mixture of silica gel and γ-Al_2O_3 and use the procedure described in the Experimental section to deposit the oleic acid and dye molecule. Next, the sample is placed under the microscope with a 10X objective and illuminated with the pulsed laser radiation. For particle (1), the spectrum is shown in

Figure III, and we can identify this particle as γ-Al_2O_3. Another particle (2) gave the same spectrum, therefore, it is also γ-Al_2O_3. Figure IV shows the spectrum of particle (3) which is seen to be silica gel. Particle (4), exhibited band maxima at 599.2 and 657.8 nm which indicates silica gel. The spectrum of particle (5) shows maxima at 617.5, 642.5 and 678.0 and is therefore γ-Al_2O_3. This experiment was done using a two dimensional layer of the particles. The next experiment was performed on a pile of the mixture (three dimensional sample), and within this sample configuration, individual particles could still be identified from their characteristic spectra. This type of experiment on high surface area minerals can be used to identify individual particle surfaces utilizing the high spatial resolution of a microscope to eliminate spectral interferences of neighboring particles.

B. Micro Raman Spectroscopy

To develop a data base for the low surface area minerals, we decided to use the micro Raman spectroscopic technique because low surface area, highly crystalline (long range order) minerals exhibit large Raman signals. The vibrational Raman spectral characteristics for the minerals follows: Corundum (γAl_2O_3) 378 cm^{-1} (360 counts/sec) and 418 cm^{-1} (1800 counts/sec); Quartz - 468 cm^{-1} (2500 counts/sec.) and Gypsum - 1008.5 cm^{-1} (4500 counts/sec), where each value of the signal strength in the parenthesis was observed with the 40X microscope objective and the 488.0 nm exciting line of the Argon ion laser (63 mw at the sample).

Spectra were taken of the gypsum blank and the gypsum with the incorporated Ra and although the frequency of 1008.5 cm^{-1} was observed in all gypsum samples, there are indications that the bands have asymmetric shapes with different amounts of asymmetry relative to the natural gypsum. Therefore, the micro Raman spectra can be used to identify specifically doped surfaces. We have recently studied $BaSO_4$ samples from commercial sources and freshly prepared in the laboratory with the micro Raman system. The commercial sample gave the literature value for the SO_4^{-2} totally symmetric vibration but the freshly prepared sample had a shifted frequency. In the same series of experiments, we observed the micro Raman spectra of two samples $BaSO_4$ with K and with Fe atoms incorporated in the $BaSO_4$ crystals. The K and Fe doped samples gave Raman spectra with the same frequency for the SO_4 vibration but a close examination of the spectral contour revealed specific asymmetries in the bands. It seems likely that, with proper band contour analysis, a correlation can be made between band contour and specific dopant concentration. In the present study, we have observed the band contour differences between the gypsum samples, and we attribute these differences to the presence of the dopant on the surface.

In Figures Va,b,c, we show results of a series of experiments on the mixture of quartz, corundum and gypsum (Ra). The mixture contains 0.5 mg of gypsum (Ra), 4 mg of quartz and 5 mg of corundum. For the experiment, a 0.5 mg random sample was taken and placed on the microscope stage. This amounts to

approximately 30 micrograms of gypsum in the mixture. In order to find the gypsum we set the spectrometer to the vibrational Raman shift 1008.5 cm^{-1} and within two to three minutes, we identified a gypsum particle. (Figure Va). Particle 2 can be identified as quartz (Figure Vb) and particle 3 is corundum (Figure Vc). Using this technique, particles that exhibit long range order in the crystal lattice can be identified quite easily since they give very strong Raman signals.

Section IV - Conclusion

We have performed both micro fluorescence and micro Raman spectroscopies on a variety of minerals with the goal of surface identification. The present experimental results show that the micro fluorescence technique of a mineral sample doped with a dye molecule can identify a specific surface as long as the mineral sample has a high surface area (200-600 m^2/g). When the surface area is low, approximately $2m^2/g$, the micro Raman technique proved to be the superior technique in identifying the surface. To extend the micro fluorescence technique to include the identification of low surface area minerals, new surfactants should be found so that the concentration of the probe molecule can be increased on the surface. Such surfactants must be able to interact strongly with the surface and at the same time project multiple sites to bind for the aromatic dye molecule. Once the proper surfactant has been found, the technique outlined in the present study can be followed and a positive identification of the low surface area mineral can be made. Therefore, by using the micro fluorescence and the micro Raman technique, we have identified all of the minerals listed in the statement of work for this contract.

Table I

Emission Spectra

Deutroporphyrin IX Dimethyl Ester (DPDE) in 1,2 Dichlorothane (1.0×10^{-4} M)

λ_{max} (nm)	622.5	650.0	686.5

DPDE in Oleic Acid (1.0×10^{-4} M)

λ_{max} (nm)	627.5	644.5	688.4

DPDE on Silica Gel (Dry deposition) with mineral oil added after vacuum drying:

λ_{max} (nm)	597.8	660.4

DPDE on γ-Al_2O_3 (Dry deposition) with mineral oil added after vacuum drying:

λ_{max} (nm).	617.8	643.0	681.8

DPDE on Silica Gel with Oleic acid added first to the Silica Gel:

λ_{max} (nm)	599.2	657.8

DPDE on γ-Al_2O_3 with Oleic acid added first to the γ-Al_2O_3:

λ_{max} (nm)	617.5	642.5	678.0

DPDE on crystalline quartz with the oleic acid added first to the sample:

λ_{max} (nm)	623.0	645.5	689.0

DPDE on αAl_2O_3 (corundum) with the oleic acid added first to the sample:

λ_{max} (nm)	622.5	646.0	688.5

DPDE on Gypsum + oleic acid (added first)

λ_{max} (nm)	621.8	644.9	688.5

DPDE on Gypsum (blank run) + oleic acid (added first):

λ_{max} (nm)	622.3	644.4	686.5

DPDE on Gypsum (^{226}Ra incorporation) + oleic acid (added first):

λ_{max} (nm)	622.8	644.4	687.5

Table II

Temporal Data

Sample	Lifetime at the specified (wavelength) in nanoseconds	Time delay of fluorescence maxima relative to the laser pulse (nanoseconds)	Percent loss of signal per minute
Deutroporphyrin in Dichlorgethane (1.0×10^{-4} m)	14.5±1.7(623.0 nm) 13.2±0.42(685.0 nm)	8.5 9.1	- -
Deutroporphyrin in Oleic acid (1.0×10^{-4} M)	19.9±2.9(623.0 nm)	5.2	-
Silica Gel + dye + mineral oil	9.1±1.2(600.0 nm) 7.8±0.45(660.0 nm)	2.0 2.4	3.0
γAl_2O_3 + dye + mineral oil	8.5±1.3(615.0 nm) 7.0±0.42(645.0 nm)	4.8 3.2	13.7
Silica Gel + oleic acid + dye	6.3±1.3(600.0 nm) 4.9±1.6(660.0 nm)	1.6 2.0	3.6
γAl_2O_3 + oleic acid + dye	8.9±1.2(618.5 nm) 5.1±0.8(640.0 nm)	3.2 2.4	3.4
Quartz + oleic acid + dye	19.6±3.0(623.0 nm) 9.1±0.76(648.0 nm)	7.0 6.7	2.34
Corundum + oleic acid + dye	25.6±3.0(623.0 nm) 14.2±2.2(650.0 nm)	6.0 3.6	2.0
Gypsum blank + oleic acid + dye	22.5±4.3(623.0 nm) 9.3±1.8(650.0 nm)	5.6 4.0	2.9
Gypsum (^{226}Ra) + oleic acid + dye	18.9±1.8(623.0 nm) 7.5±0.5(658.0 nm)	5.6 4.8	1.8

Figure I Fluorescence Spectrum
Silica Gel (oleic acid + dye)

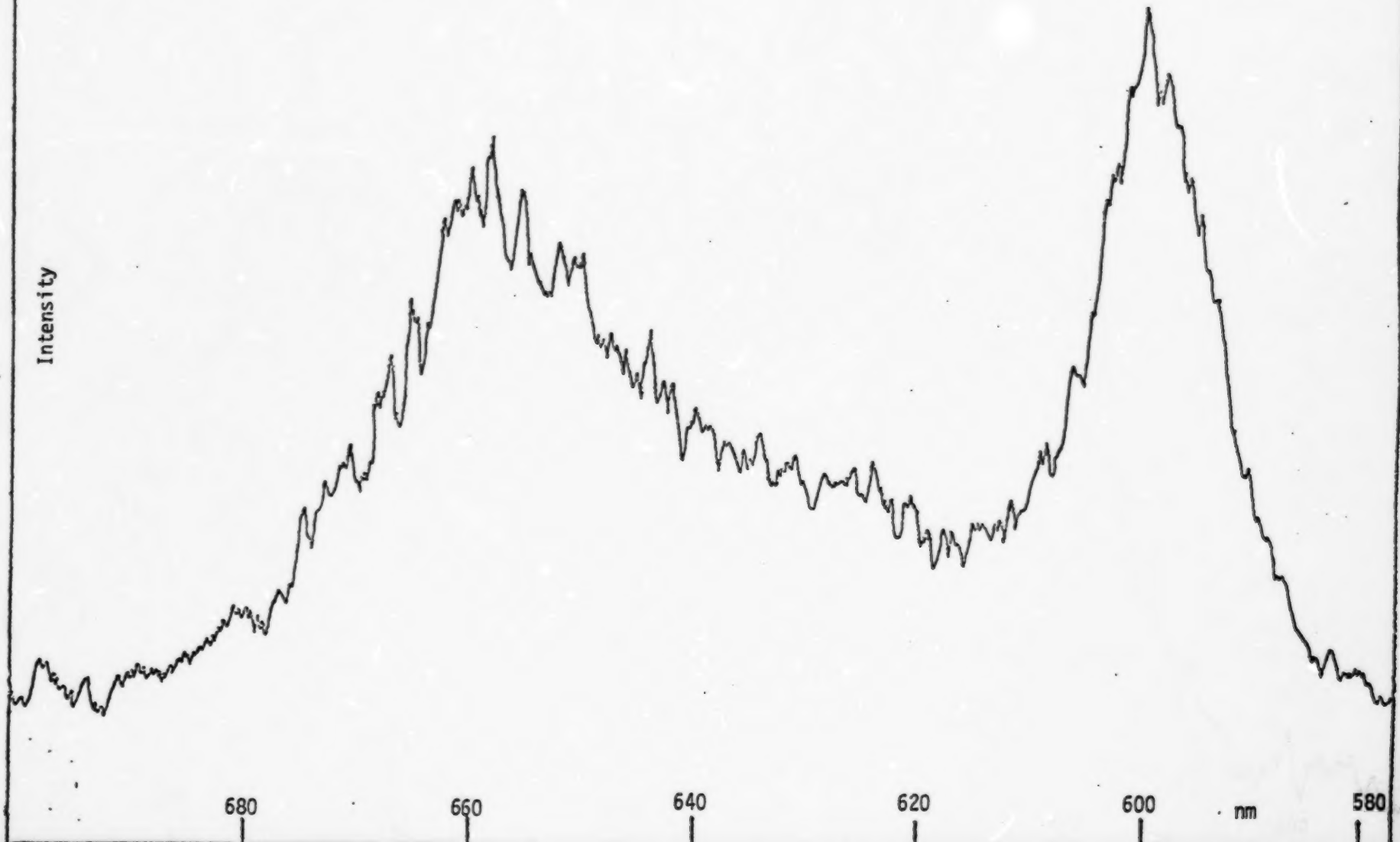


Figure II Fluorescence Spectrum
γ Al_2O_3 (oleic acid + dye)

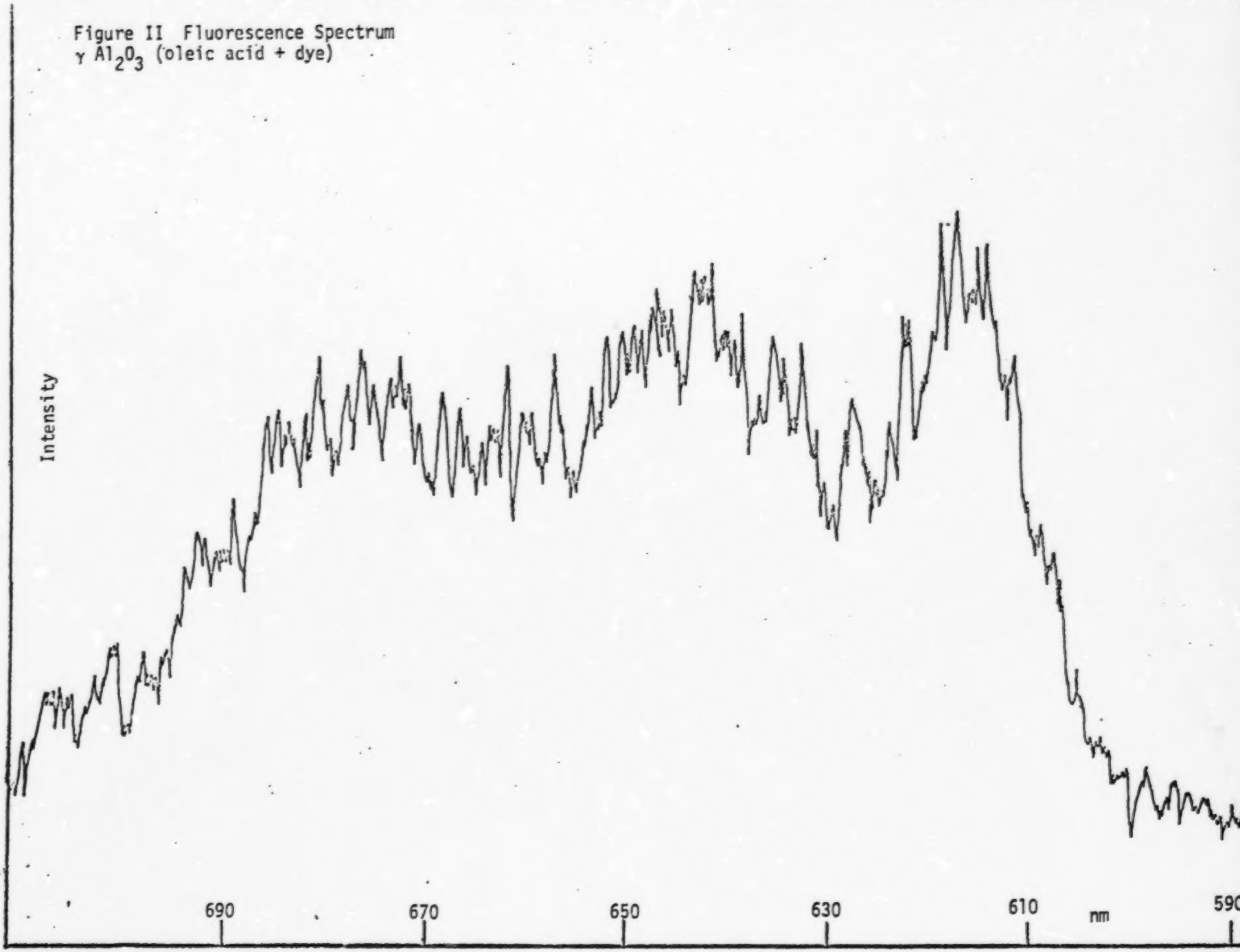


Figure III Fluorescence Spectrum
Particle (1)

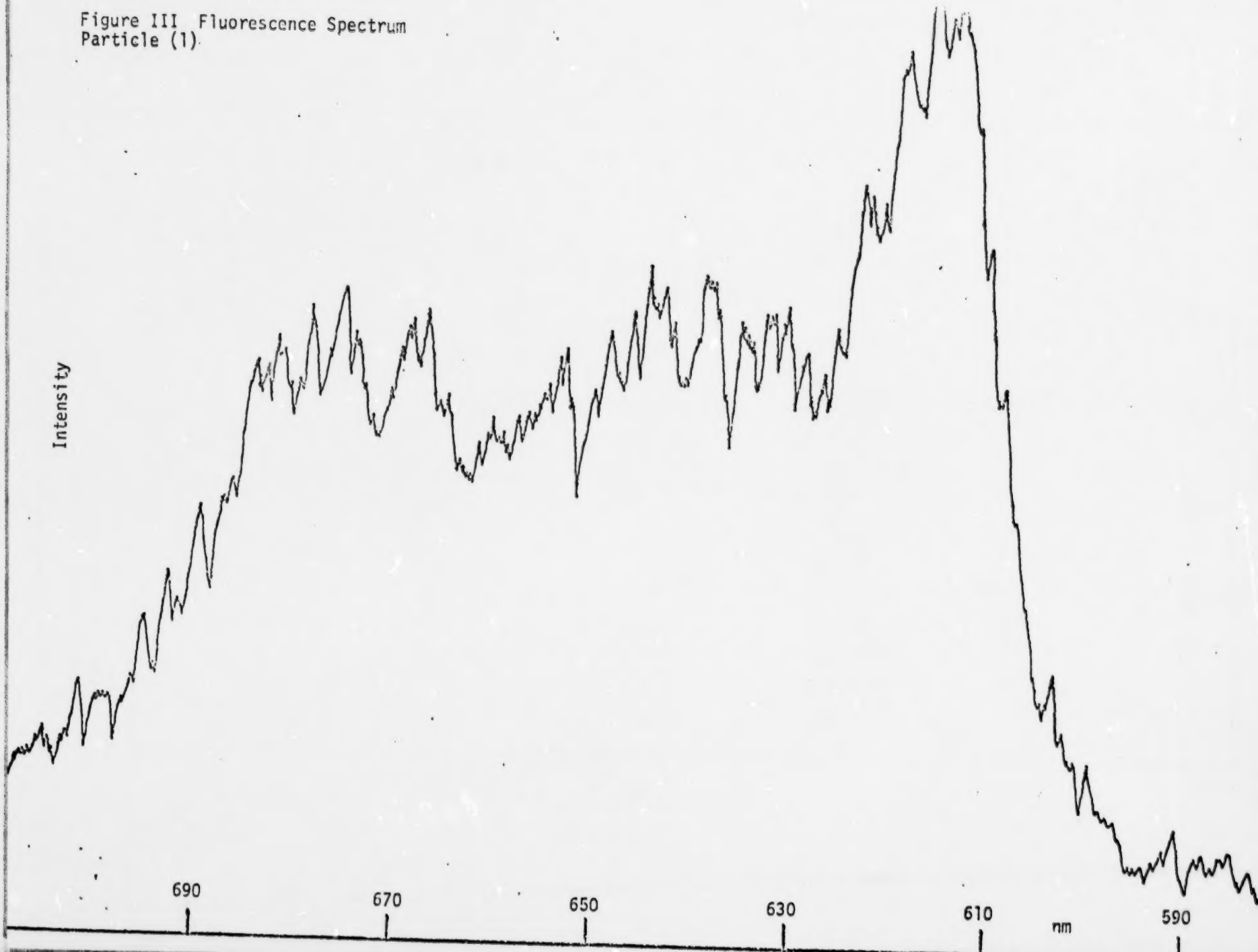


Figure IV. Fluorescence Spectrum
Particle (3)

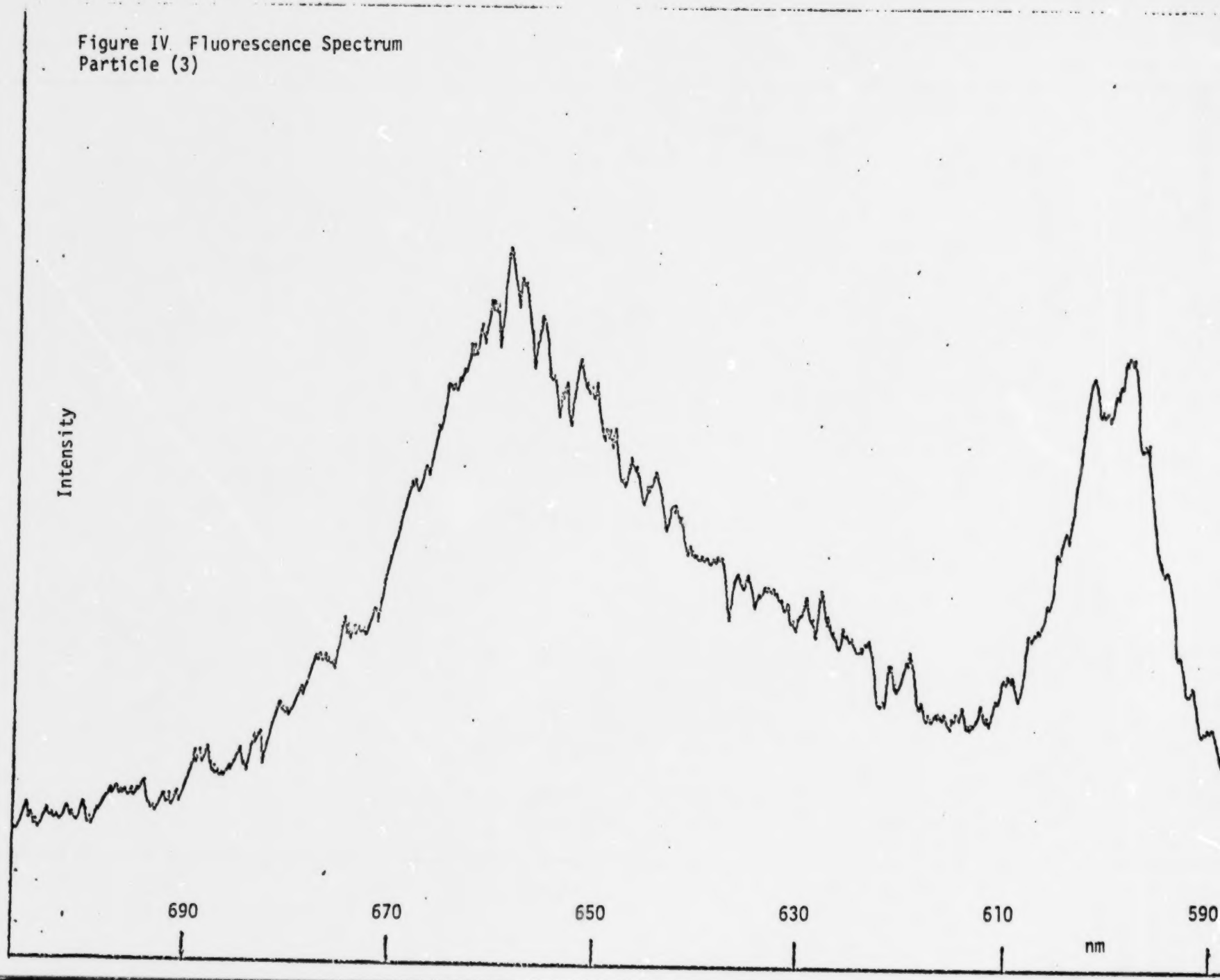


Figure Va Raman Spectrum
Gypsum Particle

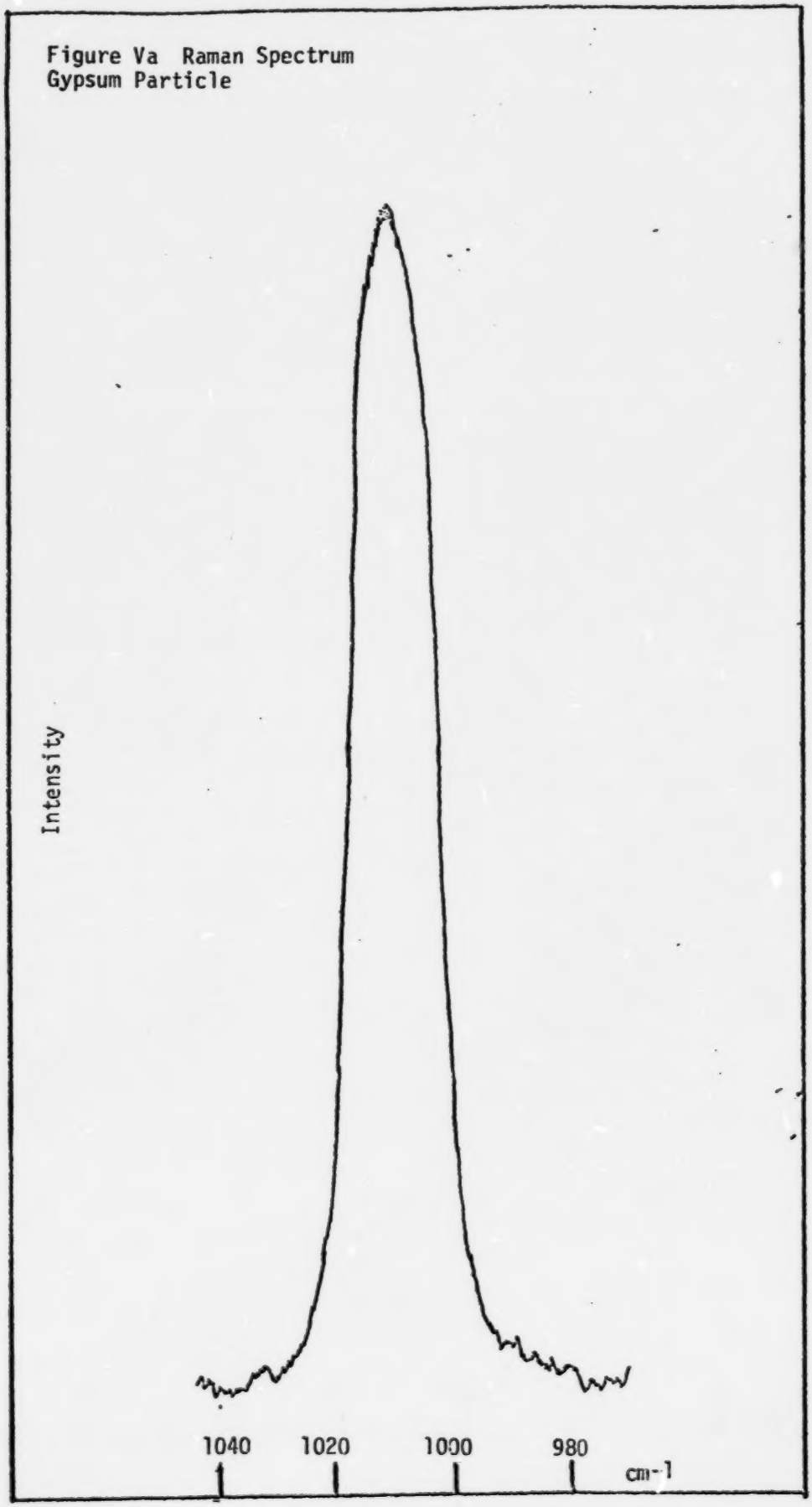


Figure Vb Raman Spectrum
Quartz Particle

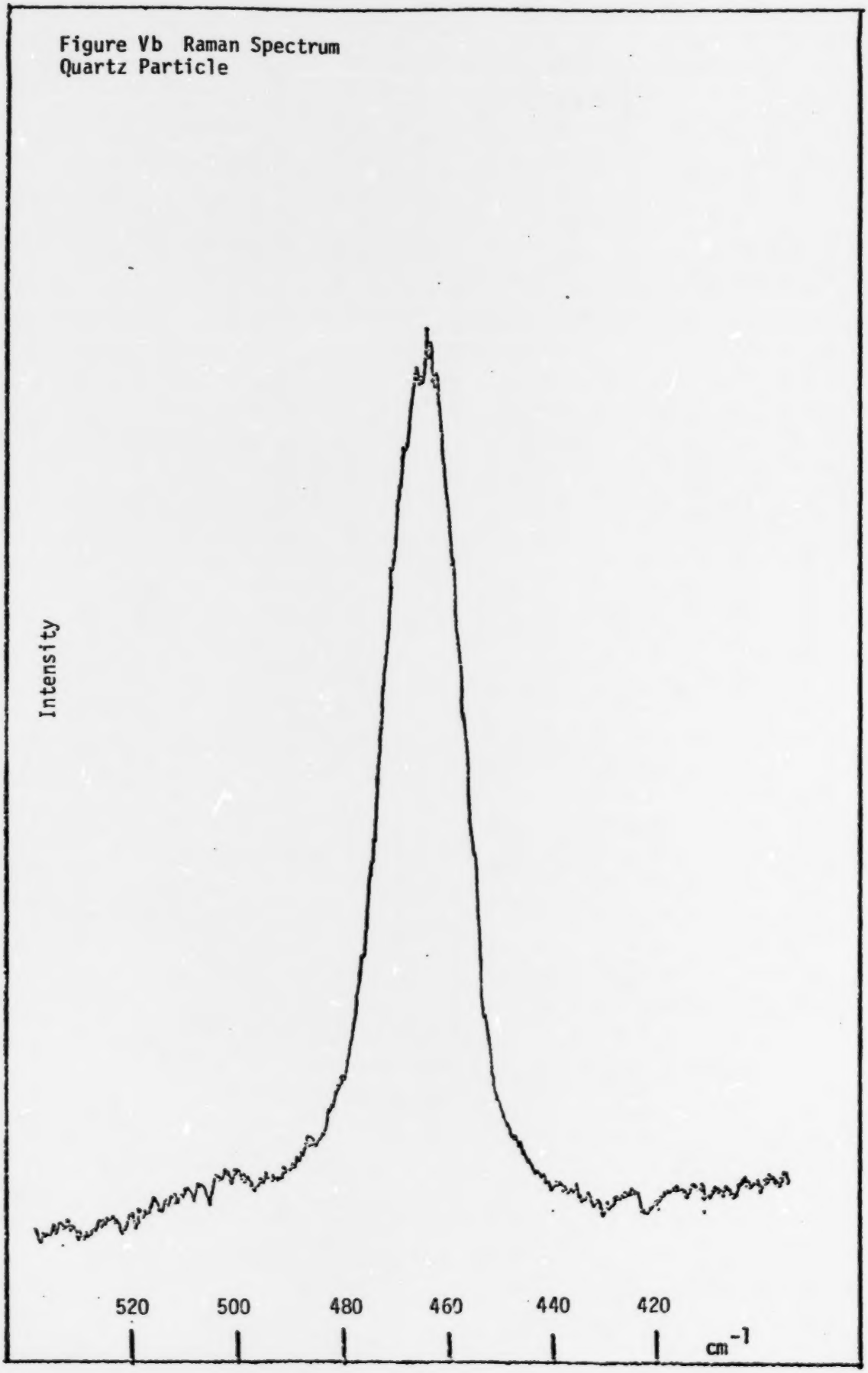
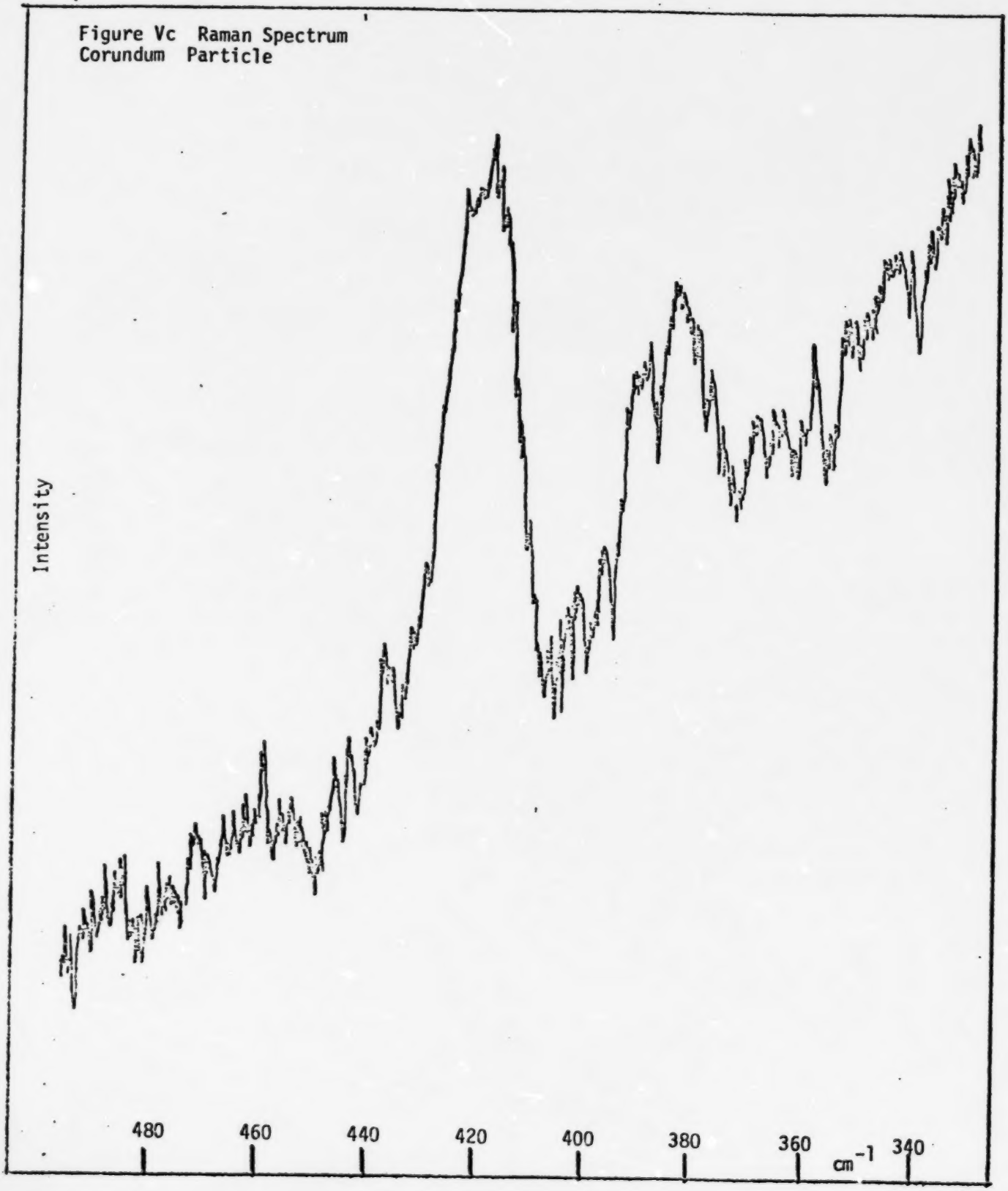


Figure Vc Raman Spectrum
Corundum Particle



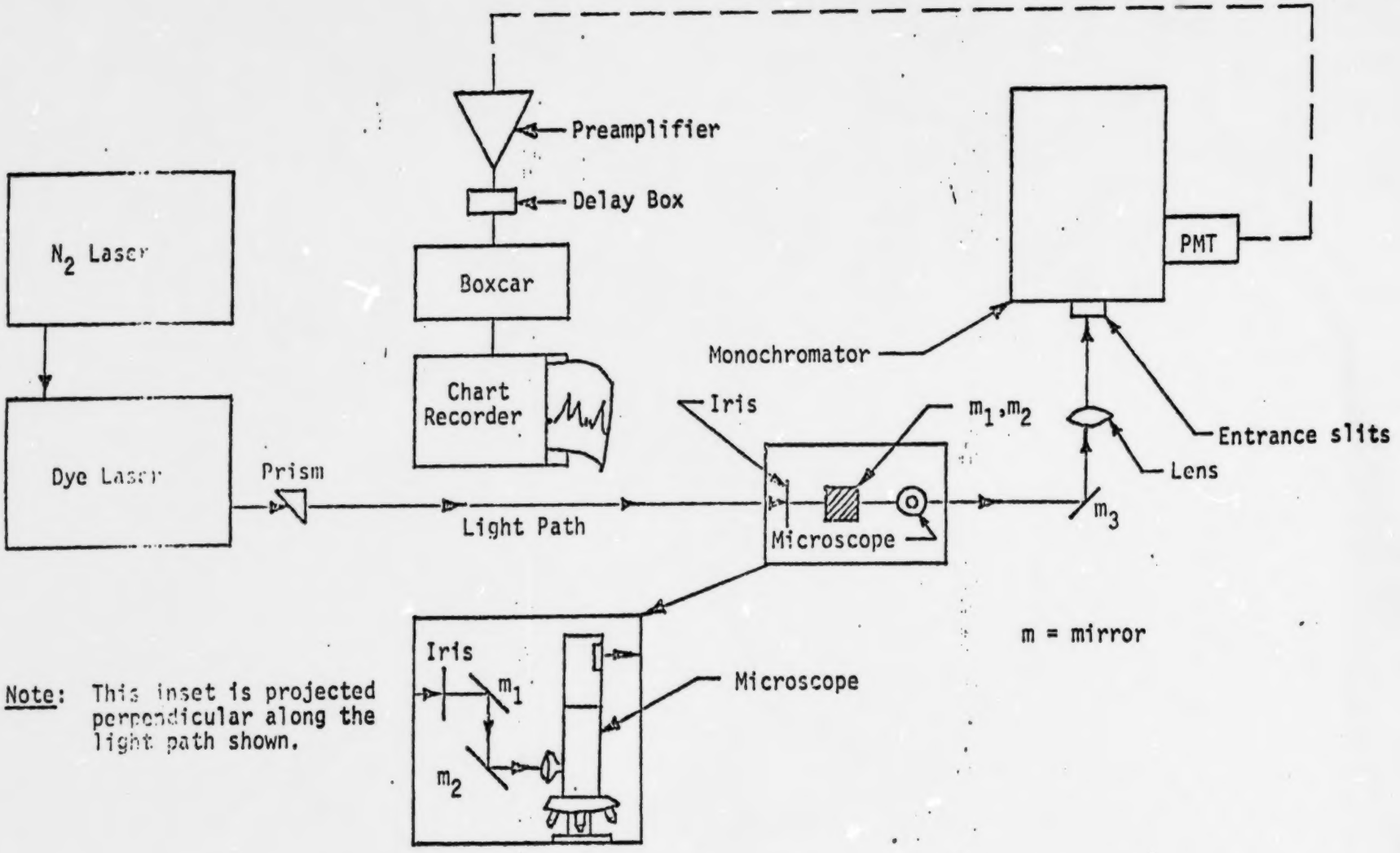


Figure VI Schematic diagram of experimental set-up.